

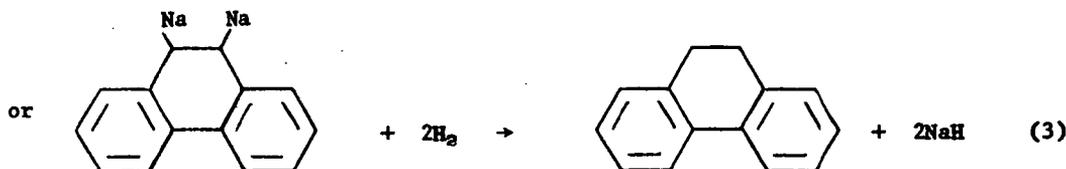
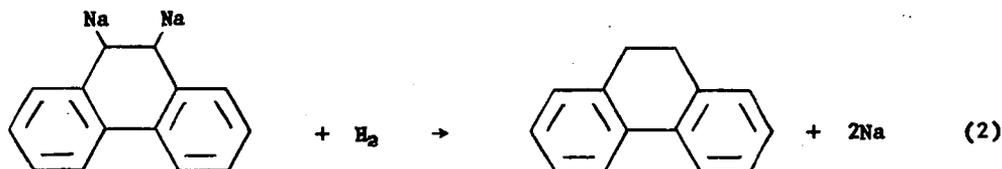
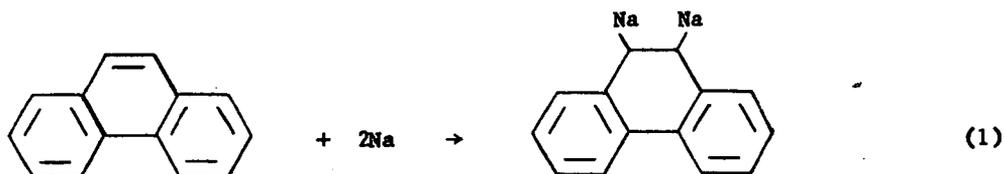
Presented Before the Division of Fuel Chemistry  
 American Chemical Society  
 Chicago, Ill., Aug. 30-Sept. 4, 1964

ALKALI METALS AS HYDROGENATION CATALYSTS FOR AROMATIC MOLECULES  
 Sidney Friedman, Marvin L. Kaufman, and Irving Wender

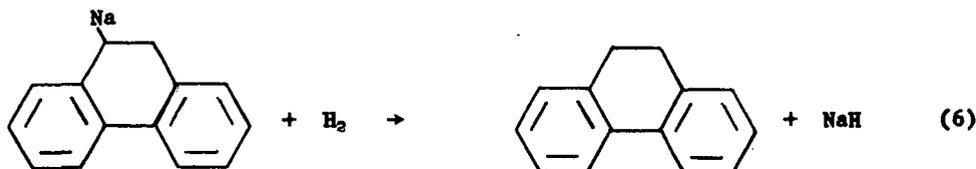
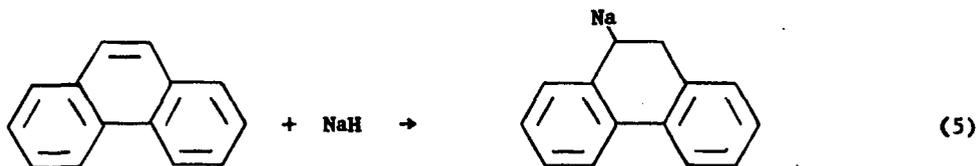
U. S. Bureau of Mines, 4800 Forbes Avenue  
 Pittsburgh, Pa. 15213

Sodium in liquid ammonia has been used for many years as a reducing system for aromatic systems,<sup>1,8/</sup> and more recently both sodium and lithium in amines have become increasingly important.<sup>3,4/</sup> In these reductions, the amines serve as proton donors; in liquid ammonia, an alcohol is usually added to furnish the hydrogen.<sup>1/</sup> There are also a few cases known where ethers are used as solvents for reductions with alkali metals;<sup>5,6/</sup> in these reactions, the alkali metal salt of the hydrocarbon is undoubtedly formed. Addition of water or alcohol then provides the necessary hydrogen to decompose the salt and form the reduced hydrocarbon. In every one of these reactions, the alkali metal is used stoichiometrically, and is eventually converted to  $M^+ B^-$ , where  $M = Na$  or  $Li$  and  $B = OH, OR, \text{ or } NR_2$ . In each of these reactions, the equivalent of an ionic carbon-metal bond is formed at some stage of the reaction.

Carbon-metal bonds, such as those formed in alkali metal reductions, are known to be readily hydrogenated.<sup>7/</sup> Thus, if such a bond is formed in an atmosphere of hydrogen, reduction can take place to regenerate the metal or to form its hydride.



The sodium hydride formed in (3) or (4) might also be capable of adding to a double bond, providing an alternate pathway to the reduction product.



In either case, the series of reactions would constitute a catalytic hydrogenation.

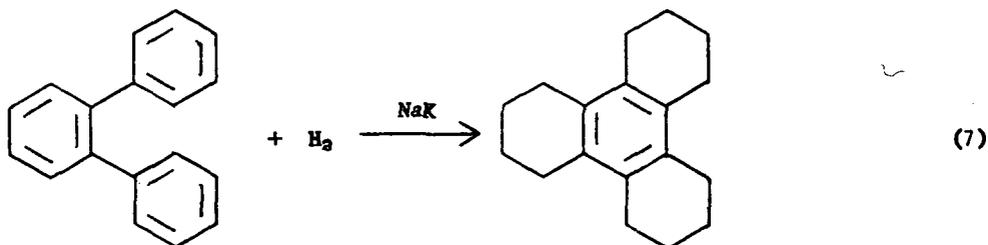
Several investigations have been carried out to explore this catalytic system, using both alkali metals<sup>8-10/</sup> and sodium hydride<sup>11/</sup> as the initial catalysts, and in all cases hydrogenations have been achieved. However, very little has been done toward exploring this system in detail; most of the reported work has been confined to the reduction of naphthalene to tetrahydronaphthalene. We wished to investigate the system in more detail; to study the effects of other alkali metals and of other solvents and to apply it to compounds other than naphthalene, especially compounds of the type one might find in coal or coal tar.

Initially, a series of reactions was conducted in which an alkali metal, an aromatic hydrocarbon, and a solvent (benzene or toluene) were heated with hydrogen in a rocking autoclave to a specified temperature. As an example, 10 grams of naphthalene, 1 gram of sodium, and 80 ml of toluene were placed in an autoclave with hydrogen at 1,000 psi and heated to 300° C with rocking. After five hours at temperature, the autoclave was allowed to cool overnight and then opened. The reaction product contained some white solid in suspension. Addition of isopropyl alcohol caused considerable reaction, with the evolution of gas, presumed to be hydrogen from decomposition of sodium hydride. The solution was extracted with water, and solvent removed from the organic layer by distillation. Examination of the product by mass spectrometry and gas chromatography showed it to be 62 percent tetrahydronaphthalene and 36 percent unreacted naphthalene, with 2 percent of dihydronaphthalene.

Similar experiments showed that lithium, which is a better reducing agent than sodium in metal-amine systems,<sup>4/</sup> is a much poorer catalyst than sodium for hydrogenation. Even at 325° C, only 4 percent of the naphthalene was reduced.

Further experiments with sodium at 250° gave reductions of anthracene and phenanthrene to mixtures of dihydro- and tetrahydro-derivatives. There was evidence that careful control of temperature and pressure might allow the hydrogenation to be carried out selectively.

Experiments using sodium were extended to an investigation of sodium-potassium alloy (NaK) as a catalyst. This was found to be more active than sodium, the alloy probably behaving more like potassium. At 250° C, naphthalene is reduced to tetrahydronaphthalene in 92 percent yield, with 8 percent of 1,2,3,4,1',2',3',4'-octahydro-2,2'-dinaphthyl being formed by reductive dimerization. Anthracene and phenanthrene are reduced mainly to their symmetrical octahydro derivatives, with small amounts of intermediate reduction products also being present among the products. Chrysene is reduced to a mixture of products, chief among them being hexahydro-, octahydro-, and dodecahydrochrysenes. The major reduction product of triphenylene is sym-dodecahydrotriphenylene. Both pyrene and naphthacene, however, are reduced only to the dihydro stage at 250° C. At 350° C, pyrene is reduced to a mixture of products including hexahydro- and decahydropyrenes. At 350° C, biphenyl is hydrogenated to phenylcyclohexane in good yield and p-terphenyl yields both trans-1,4-diphenylcyclohexane and dodecahydroterphenyl, corresponding to the reduction of either one or two of the three rings. The reduction of o-terphenyl is similar, except that cyclization occurs to give sym-dodecahydrotriphenylene as a major product.



This is probably the best available method for preparation of the latter compound.

In the reduction of the polyaryls, scission of the bonds between the rings is indicated by the formation of benzene, biphenyl, phenylcyclohexane, and traces of higher polyaryls. When benzene or toluene is heated to 350° C with NaK and hydrogen, hydrogen is absorbed with the formation of hydrogenated dimers and higher polymers, as well as coal-like chars.

Since the reaction of alkali metals and alkali metal salts is an equilibrium reaction,



it was felt that NaK could be formed in situ in a reaction vessel at elevated temperatures by using sodium metal and the appropriate potassium salt. Potassium chloride-sodium mixtures fail to give results comparable to NaK when used as a hydrogenation catalyst at 250° C. Instead, the mixture behaves like sodium. When potassium carbonate or hydroxide is used with sodium, however, hydrogenation of naphthalene, phenanthrene, and pyrene proceeds to give products and yields similar to those obtained with NaK.

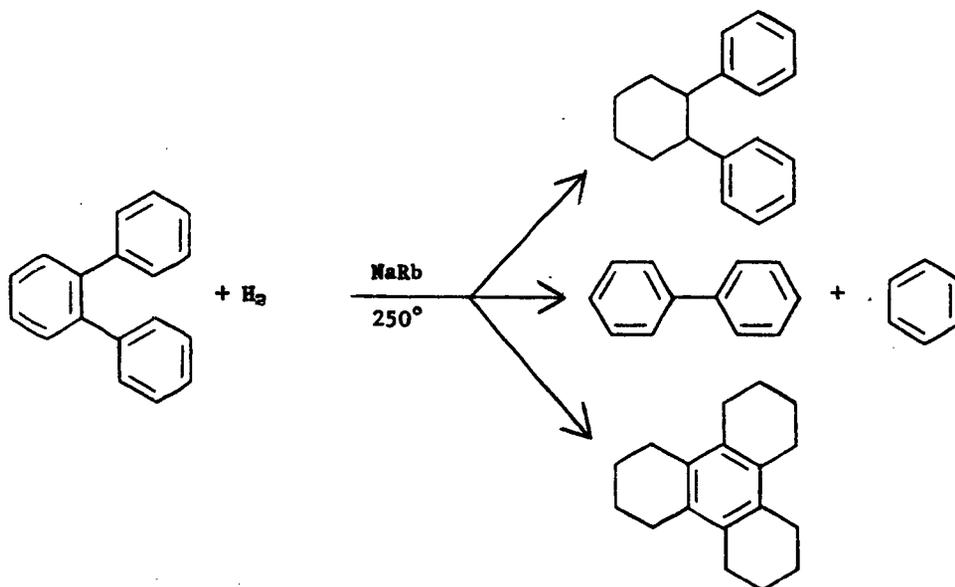
The success of the potassium salt/sodium metal system suggested that the use of rubidium salts might allow the catalytic behavior equivalent to sodium-rubidium (NaRb) to be studied without the inconvenience of handling metallic rubidium. Experiments have indicated this to be the case.

At 180° C, naphthalene is hydrogenated to tetrahydronaphthalene in 99 percent yield when a mixture of sodium metal and rubidium carbonate is used as catalyst. At temperatures between 200° C and 220° C, anthracene and phenanthrene are rapidly hydrogenated to their octahydro derivatives. Chrysene is hydrogenated to dodecahydrochrysene, i.e., a product containing a single aromatic ring, in 85 percent yield at 250° C. Perylene, at 250° C, is reduced to a mixture of 47 percent octahydroperylene and 30 percent dodecahydroperylene; pyrene similarly forms decahydro- and dodecahydroperyrenes. Naphthacene, which is strangely resistant to extensive reduction by this method, nevertheless goes to octahydronaphthacene in 36 percent yield at 300° C.

Fluorene, which seems to have been neglected in the literature on catalytic hydrogenation, is reduced by NaRb to hexahydrofluorene. A smaller amount of tetrahydrofluorene was isolated from a chromatogram and identified by its ultraviolet spectrum.

Both biphenyl and 1,3,5-triphenylbenzene are reduced catalytically by NaRb. Biphenyl forms phenylcyclohexane in greater than 70 percent yield at 250° C. This is comparable to a reduction catalyzed by NaK at 350° C. Triphenylbenzene is hydrogenated and also cleaved to give a mixture of products. These include hexahydro-, dodecahydro-, and octadecahydrotriphenylbenzene, as well as hydrogenated biphenyl and terphenyl.

o-Terphenyl, at 250°, forms both hexahydroterphenyl and sym-dodecahydrotriphenylene, the cyclization product. The most important product, however, is biphenyl, formed as a result of cleavage.



(9)

It thus appears that polyaryls are cleaved under these experimental conditions. In addition, small but measurable quantities of biphenyl appear to be formed by dimerization of the benzene used as solvent, while toluene dimerizes to give ditolyl and methylbiphenyl, the last by loss of a methyl group.

The presence in an aromatic molecule of oxygen-containing functional groups necessitates that sufficient catalyst be present to allow for the formation of an alkali metal salt of the hydroxyl group which may be formed. The major product formed in the NaRb catalyzed hydrogenation of 2-methoxynaphthalene is tetrahydronaphthalene with small amounts of 2-naphthol, dihydronaphthol, and tetrahydronaphthol as other important products. 2-Naphthol, at 220°, is hydrogenated to tetrahydronaphthalene, with a small amount of tetrahydronaphthol being formed, also. p-Phenylphenol, at 250°, forms phenylcyclohexane as the major product. 2-Naphthoic acid, also at 250°, is reduced and decarboxylated to tetrahydronaphthalene.

The reduction of anthraquinone at 250° also demonstrates that NaRb removes oxygen from organic compounds at elevated temperature and hydrogen pressure. In this case, octahydroanthracene is the principal product, with sym-octahydroanthranol as the only other important product.

Diphenylene oxide is converted primarily to phenylcyclohexane at 250° with small amounts of biphenyl and hexahydroterphenyl. This last product again indicates involvement of the solvent benzene.

In contrast to the reactivity of diphenylene oxide, dibenzothiophene, its sulfur analog, is relatively inert toward both hydrogenation and cleavage in the presence of NaRb. At 250°, some phenylthiophenol and biphenyl are formed, but most of the dibenzothiophene is recovered unchanged. This is also in contrast to Raney nickel or lithium-ethylenediamine reductions, both of which bring about desulfurization. The presence of sulfur compounds does not poison the alkali metal catalysts, and this is one important factor in their favor.

When nitrogen-containing heterocyclic aromatic compounds were hydrogenated, some ring cleavage and decomposition was noted. Pyridine, when used as a solvent, forms a variety of products, including tar. Quinoline with NaRb at 220°, is hydrogenated to tetrahydroquinoline, but at the same time it forms large quantities of dimers, in addition to a considerable number of unidentified products. Acridine and phenanthridine, at 250°, are hydrogenated to octahydro derivatives, apparently the unsymmetrical isomers.

Experiments to evaluate cesium as a catalyst were carried out in a manner similar to those involving rubidium, using cesium carbonate and sodium metal. Cesium proved to be a less active hydrogenation catalyst than rubidium, or about equal to potassium in catalytic activity.

Initially, benzene and toluene were used as solvents because of their lack of activity toward alkali metals. Since the work was directed primarily toward reductions of coal, it was apparent that a better coal solvent would be useful. Amines, which are good coal solvents, react with alkali metals to form amides:



However, the reaction is probably reversible, so that in the presence of hydrogen, some metal remains, probably in solution. In any event, the catalytic hydrogenation does proceed in amine and in benzene-amine solvents. Whereas 180° is the lowest temperature at which measurable hydrogen uptake occurs with benzene as solvent, at 120° phenanthrene is hydrogenated to octahydrophenanthrene in ethylenediamine and in butylamine-benzene (1:1) with sodium and rubidium carbonate catalyst. By lowering the initial hydrogen pressure to 100 psi it is possible to prepare 1,2,3,4-tetrahydrophenanthrene in butylamine-benzene at 120°.

Similarly, other polycyclic hydrocarbons can be reduced at temperatures up to 200° in ethylenediamine and in ethylenediamine-benzene (1:1). In ethylenediamine, pyrene can be hydrogenated to a mixture containing tetra-, hexa-, and decahydro-pyrenes; in ethylenediamine-benzene, naphthacene is converted to a mixture of di-, hexa-, and octahydronaphthacenes. These results are roughly comparable to those obtained at 250° when benzene is used as solvent.

The use of alkali metals as catalysts for hydrogenation of coal tar and its fractions and of coal itself is currently under investigation. For example, a pitch which originally had a  $H_{\text{arom}}/H_{\text{aliph}}$  ratio of 4.26 was hydrogenated in toluene at 250°, using NaRb as catalyst. This ratio was reduced from 4.26 to 0.75. At 350°, in the absence of solvent, the ratio of  $H_{\text{arom}}/H_{\text{aliph}}$  was further reduced to 0.61.

### Experimental

Reagents. The hydrocarbon solvents were dried over sodium. The ethylenediamine was refluxed with sodium and freshly distilled before use.

The reactants were obtained from standard suppliers. Where possible, reagent grade material was used.

The NaK (containing 76 percent potassium by weight) was generously provided by the Mine Safety Appliance Research Corp. The liquid NaK was transferred by means of a hypodermic syringe.

Analyses of products. Products were analyzed by gas-liquid chromatography where possible, and by low-voltage mass spectrometry routinely. This latter procedure provides a molecular weight distribution of products. In certain experiments, it was possible to isolate a specific component and identify it by infrared and ultraviolet spectrometry.

The procedure for all experiments was similar. Several examples will be given to illustrate the procedure. Results are tabulated in tables I-V.

#### Hydrogenation of Naphthalene

A solution of 30 grams of naphthalene in 150 milliliters of toluene was placed in an 0.5 liter Aminco rocking autoclave with 2 grams of NaK. The autoclave was pressured to 1,250 psig with hydrogen, and then heated to 250° C. It took 2-1/2 hours for the autoclave to reach this temperature. The autoclave was kept at 250° for 4-1/2 hours. The autoclave was allowed to cool overnight and isopropyl alcohol added to decompose the residual NaK and metal hydrides. The solution was

extracted with water to remove the sodium and potassium hydroxides, and the organic layer extracted with ether. The ether solution was distilled through a Helipack packed column to remove all solvents. The residue, containing the naphthalene and its reduction products, was examined by mass spectrometry and gas chromatography. It was found to consist of 91 percent tetrahydronaphthalene and 8 percent of dimeric products of molecular weights 260 and 262.

#### Hydrogenation of Phenanthrene

A solution of 5 grams of phenanthrene in 80 milliliters of benzene was placed in an Aminco rocking autoclave with 1.5 grams of sodium and 2.0 grams of rubidium carbonate. The autoclave was pressured to 1,400 psig with hydrogen, and then heated to 200° C. It took two hours for the autoclave to reach this temperature, which was maintained for 5 hours. The autoclave was allowed to cool overnight, and isopropyl alcohol added to decompose the metal hydrides. The solution was extracted with water to remove the metal hydroxides, and the organic layer extracted with ether. The ether and benzene were removed by distillation and the residue was examined by mass spectrometry. The product contained 10 percent dihydrophenanthrene and 78 percent octahydrophenanthrene, as well as smaller amounts of tetrahydrophenanthrene and phenanthrene. Traces of dimeric products were also present.

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Table I. Alkali metal catalyzed hydrogenations of polycyclic aromatic hydrocarbons

Compound	Catalyst	Temp., °C	Principal products <sup>a/</sup>
Naphthalene	Li	325	Very little hydrogenation
	Na	300	Tetrahydronaphthalene
	NaK	250	Tetrahydronaphthalene
	NaRb	180	Tetrahydronaphthalene
Anthracene	Na	250	Dihydro-, tetrahydroanthracene
	NaK	250	Octahydro-, tetrahydroanthracene
	NaRb	220	Octahydroanthracene
Phenanthrene	Na	250	Tetrahydro-, dihydrophenanthrene
	NaK	250	Octahydrophenanthrene
	NaRb	200	Octahydrophenanthrene
Naphthacene	NaK	250	Dihydronaphthacene
	NaRb	300	Octahydronaphthacene
Chrysene	NaK	250	Hexahydro-, octahydro-, dodecahydrochrysene
	NaRb	250	Dodecahydrochrysene
Triphenylene	NaK	250	Dodecahydrotriphenylene
Pyrene	NaK	250	Dihydropyrene
	NaK	350	Decahydro-, hexahydropyrene
	NaRb	250	Decahydro-, dodecahydropyrene
Perylene	NaRb	250	Octahydro-, dodecahydroperylene
Fluorene	NaRb	250	Hexahydrofluorene, tetrahydrofluorene

<sup>a/</sup> In order of decreasing yield.

Table II. Alkali metal catalyzed hydrogenations of polyaryl hydrocarbons

Compound	Catalyst	Temp., °C	Principal products <sup>a/</sup>
Biphenyl	NaK	350	Phenylcyclohexane
	NaRb	250	Phenylcyclohexane
o-Terphenyl	NaK	350	sym.-Dodecahydrotriphenylene
	NaRb	250	Biphenyl, sym.-dodecahydrotriphenylene, hexahydro-terphenyl
1,3,5-Triphenylbenzene	NaRb	250	Hexahydro-, dodecahydro-, octadecahydrotriphenylbenzene, phenylcyclohexane

a/ In order of decreasing yield.

Table III. NaRb catalyzed hydrogenations of oxygenated aromatic compounds

Compound	Catalyst	Temp., °C	Principal products <sup>a/</sup>
2-Methoxynaphthalene	NaRb	250	Tetrahydronaphthalene, 2-naphthol, dihydro- and tetrahydronaphthol
2-Naphthol	NaRb	220	Tetrahydronaphthalene, tetrahydro-2-naphthol
p-Phenylphenol	NaRb	250	Phenylcyclohexane
2-Naphthoic acid	NaRb	250	Tetrahydronaphthalene
Anthraquinone	NaRb	250	Octahydroanthracene, sym.-octahydroanthranol

a/ In order of decreasing yield.

Table IV. NaRb catalyzed hydrogenations of heterocyclic aromatic compounds

Compound	Catalyst	Temp., °C	Principal products <sup>a/</sup>
Diphenylene oxide	NaRb	250	Phenylcyclohexane, biphenyl, hexahydroterphenyl
Dibenzothiophene	NaRb	250	Phenylthiophenol, biphenyl
Quinoline	NaRb	220	Tetrahydroquinoline, dimers
Acridine	NaRb	250	Octahydroacridine
Phenanthridine	NaRb	250	Octahydrophenanthridine

<sup>a/</sup> In order of decreasing yield.

Table V. NaRb catalyzed hydrogenations in amine solvents

Compound	Catalyst	Temp., °C	Solvent	Principal products <sup>a/</sup>
Phenanthrene	NaRb	120	Ethylenediamine	Octahydrophenanthrene
	NaRb	120	Butylamine- benzene (1:1)	Octahydrophenanthrene
Pyrene	NaRb	200	Ethylenediamine	Tetrahydro-, hexahydro-, decahydro-pyrene
Naphthacene	NaRb	200	Ethylenediamine- benzene (1:1)	Dihydro-, octahydro-, hexahydronaphthacene

<sup>a/</sup> In order of decreasing yield.